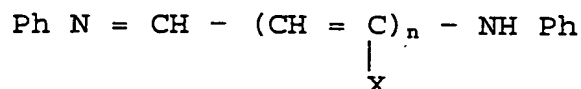


WHAT IS CLAIMED IS:

1. A process for preparing an asymmetrical indocyanine dye comprising the steps of:

a) reacting a first quaternised indolenine or substituted indolenine with a compound of the formula (II)



or hydrochloride thereof,

wherein n is 0 or 1

Ph is phenyl or substituted phenyl

X is hydrogen, halogen or alkyl, preferably chlorine, in a solvent selected from the group consisting of acetic acid, acetic anhydride and mixtures thereof in the presence of acetyl chloride, to obtain an intermediate hemicyanine, and

b) further reacting said intermediate hemicyanine with a second quaternised indolenine or substituted indolenine different from said first indolenine.

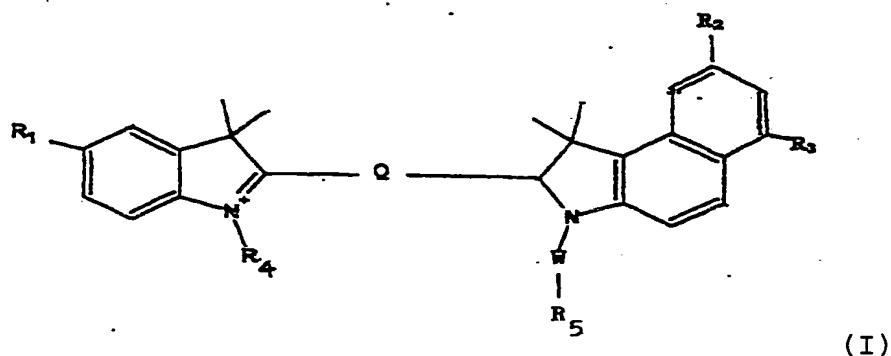
2. A process according to claim 1 wherein the amount of acetyl chloride is from 0.5 to 50% v/v, preferably from 1% to 20% v/v referred to the acetic acid/acetic anhydride solvent.

3. A process according to claim 1 wherein said first indolenine is less reactive than said second indolenine.

4. A process according to claim 3, wherein said first indolenine bears electron withdrawing groups in the benzene ring.

5. A process according to claim 3, wherein said first indolenine has additional condensed benzene rings.

6. A process according to any of claim 3, wherein said first indolenine has additional condensed benzene rings bearing sulphonic groups or is quaternised with sulfoalkyl or carboxyalkyl groups.
7. A process according to claim 1, wherein the intermediate hemicyanine from step a) is purified by extraction with a solvent suitable to extract the unreacted compounds of formula (II) without a substantial dissolution of the hemicyanine.
8. A process according to claim 7, wherein said solvent is selected from the group consisting of ethyl acetate and chlorinated organic solvents and mixtures thereof.
9. A process according to claim 8 wherein said solvent is selected from the group consisting of methylene chloride, chloroform, 1, 1, 1-trichloro ethane and mixtures thereof.
10. A process according to claim 1 for preparing an asymmetric indocyanine dye of formula:



wherein

Q is a methine bridge with 3 or 5 carbon atoms

R₁ is hydrogen, SO₃⁻ or -COOH,

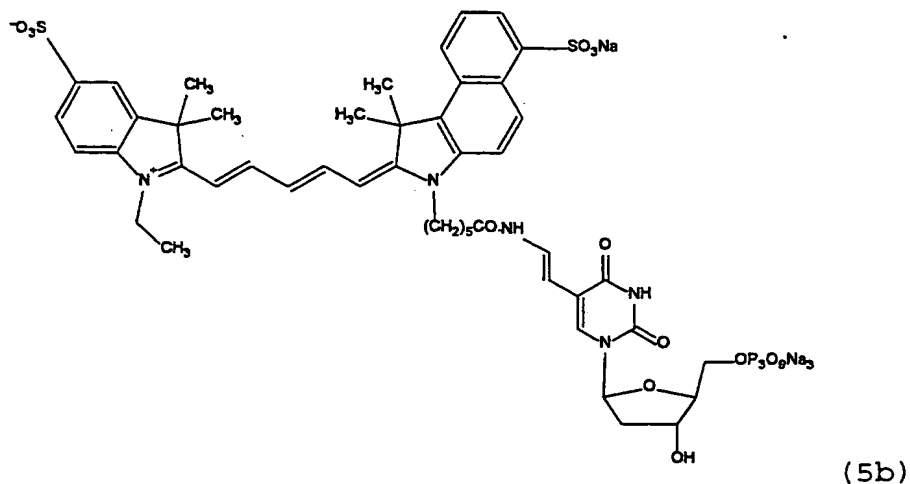
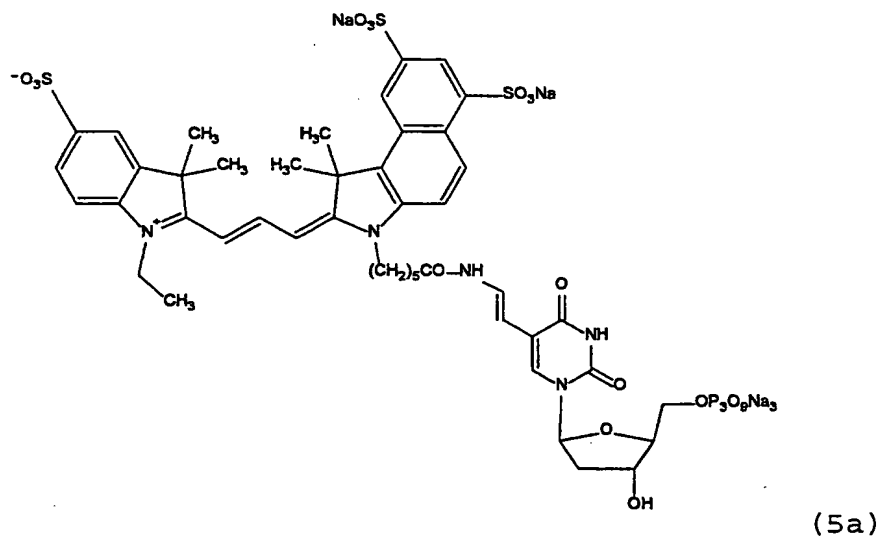
R₂ and R₃ independently are H or SO₃⁻ M⁺

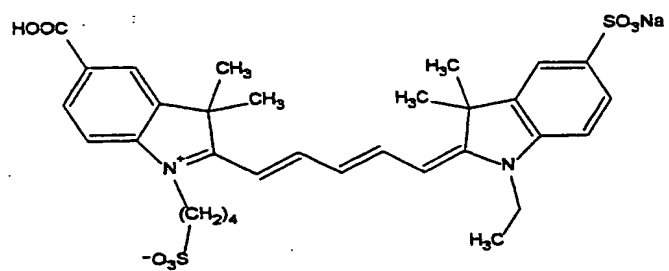
M is a monovalent metal

R₄ is C₁-C₁₂ alkyl, preferably C₁-C₄ alkyl or (CH₂)_mSO₃⁻ with m = 1 to 12, preferably 1 to 4,

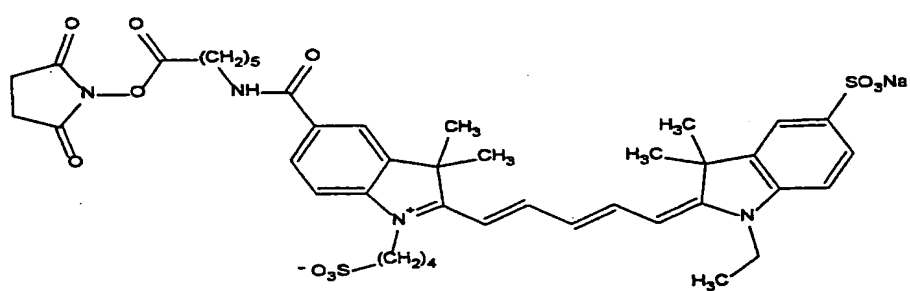
W is alkylene having from 1 to 18 carbon atoms, preferably 1 to 5 carbon atoms or is $(\text{CH}_2\text{-CH}_2\text{-O})_n \text{CH}_2\text{-CH}_2\text{-}$ wherein n is 1 to 5 and R_5 is a functional group selected from the group consisting of carboxyl, carbonyl(aldehyde), hydroxyl, amino, sulphhydryl, glycidyl, maleimide, imidazolyl carbamoyl, succinimidyl ester, phosphoramidite, isothiocyanate, anhydride, haloacetamido, sulphonyl halide, acid halide, hydrazide, phthalimidyl ester and naphthalimidyl ester.

11. A process according to claim 1 for preparing an asymmetrical indocyanine dye selected from the group consisting of:

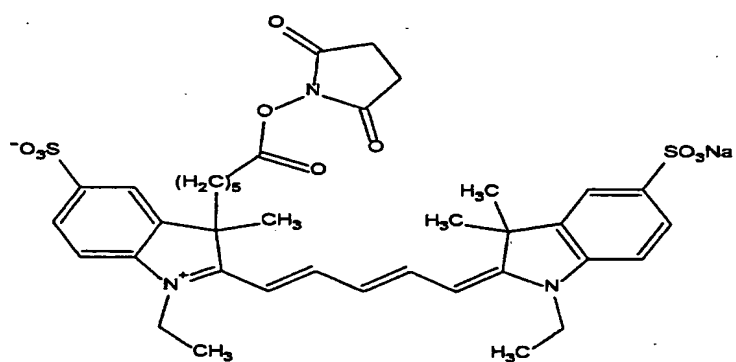




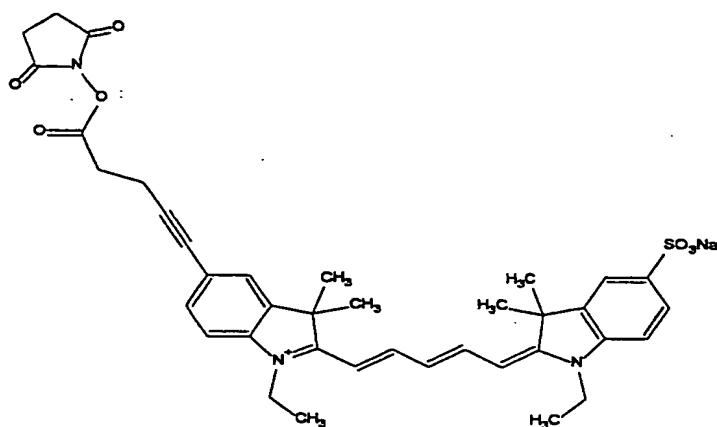
(6a)



(6b)



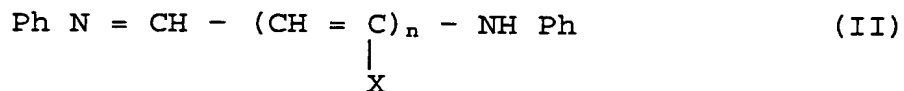
(7b)



(8b)

12. A process for preparing a hemicyanine, comprising the step of:

- reacting a quaternised indolenine or substituted indolenine with a compound of the formula (II)



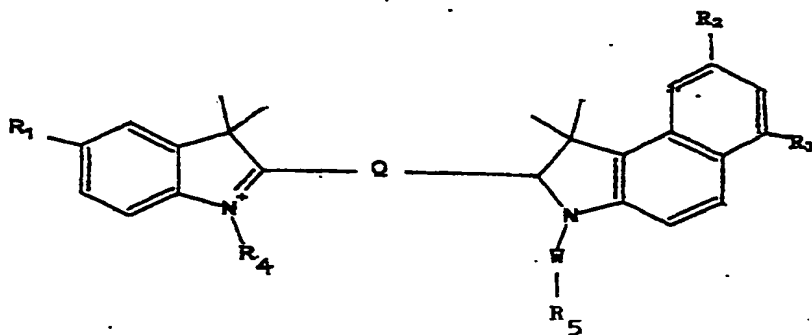
or hydrochloride thereof,

wherein n is 0 or 1

Ph is phenyl or substituted phenyl

X is hydrogen, halogen or alkyl, preferably chlorine, in a solvent selected from the group consisting of acetic acid, acetic anhydride and mixtures thereof in the presence of acetyl chloride.

13. An asymmetrical indocyanine having the formula (I)



(I)

wherein

Q is a methine bridge with 3 or 5 carbon atoms

R_1 is hydrogen, SO_3^- or $-\text{COOH}$,

R_2 and R_3 independently are H or $\text{SO}_3^- \text{M}^+$

M is a monovalent metal

R_4 is C_1 - C_{12} alkyl, preferably C_1 - C_4 alkyl or $(\text{CH}_2)_m\text{SO}_3^-$ with $m = 1$ to 12 , preferably 1 to 4 ,

W is alkylene having from 1 to 18 carbon atoms, preferably 1 to 5 carbon atoms or is $(\text{CH}_2-\text{CH}_2-\text{O})_n \text{CH}_2-\text{CH}_2-$ wherein n is 1 to 5 and R_5 is a functional group selected from the group consisting of carboxyl, carbonyl(aldehyde), hydroxyl, amino, sulphhydryl, glycidyl, maleimide, imidazolyl carbamoyl, succinimidyl ester, phosphoramidite, isothiocyanate, anhydride, haloacetamido, sulphonyl halide, acid halide, hydrazide, phthalimidyl ester and naphthalimidyl ester.

14. An asymmetrical indocyanine having the formula selected from the group consisting of

